Materials Science and Engineering A 555 (2012) 71–76

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

In situ mesophase transformation by zirconium chloride in fabrication of carbon/carbon composites

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ARTICLE INFO

Article history:
Received 15 March 2012
Received in revised form 28 May 2012
Accepted 10 June 2012
Available online 21 June 2012

Keywords:
Electron microscopy
Mechanical characterization
X-ray diffraction
Composites
Fracture
Interfaces

ABSTRACT

Carbon/carbon (C/C) composites were prepared using multiple cycle in situ mesophase densification in the presence of zirconium chloride. The mesophase transformation and the performance of C/C composites were investigated in detail. The results show that higher amount of $ZrCl_4$ and longer soaking time accelerate the condensation of aromatic hydrocarbons. Additionally, the XRD pattern and ash contents show that the $ZrCl_4$ is retained in the samples and transformed to t-ZrO_2 and m-ZrO_2 after carbonization. In all the composites, the bulk density increases with cycle times, and the flexural strength increases with bulk density. However, a decrease of flexural strength for low density composites was observed when increasing $ZrCl_4$ concentrations. This tendency is attributed to more ZrO_2 formation in the composites using 20 wt.% $ZrCl_4$. Subsequently, these ZrO_2 particles produce interface defects in the matrix which decreases its strength. Attributed to the very low content of ZrO_2 in high density composites, there is no difference between the samples using 13 wt.% and 20 wt.% $ZrCl_4$.

1. Introduction

Carbon/carbon (C/C) composites, consisting of carbon matrix reinforced with carbon fibers, are advanced materials that have widespread applications attributed to their superior mechanical properties, high thermal conductivity, low thermal expansion coefficient, combined with good frictional performance in an inert atmosphere [1,2].

Because carbon has no liquid phase under normal conditions, a carbon matrix is deposited from vapor, or through carbonization of resins or pitches, which are liquids at attainable temperatures. Impregnation of fully transformed mesophase pitch into a fiber preform is an effective way to make highly densified C/C composites in multiple cycles [3]. However, highly viscous mesophase blocks the access channels to the inner part of the preform. The extent of mesophase penetration decreases from the outer edge to the center of the composites, resulting in non-uniform filling [4]. People need a new, efficient, and low-cost process to address this issue. The concept of using in situ mesophase transformation in the fabrication of C/C composites, which fully satisfies filing requirements, was invented and developed by the Air Force Research Laboratory [4,5]. The mechanism of the process is that the capillary forces make the mixture of molten monomer (pure aromatic hydrocarbons such as naphthalene) and a catalyst easily penetrate fiber bundles or void space of the preform. When the preform is completely filled, the in situ polymerization leads the monomer to mesophase. After poly-condensation and carbonization, most mesophase pitches retained in the preform are transformed into carbon. In these works, naphthalene was usually used as the precursor monomer and aluminum chloride was the catalyst. Impregnation was efficient in filling tightly packed fiber bundles and the inner part of the preform, but $AlCl_3$ was retained in the final composite, which can influence the final composite properties [4–6].

$AlCl_3$ was one of the first and most extensively used catalysts for polymerizing aromatic hydrocarbons to prepare spinnable mesophase pitch. Mochida et al. studied the synthetic pitch produced from different feedstocks (such as pure aromatic hydrocarbons, heterocyclic compounds, and the mixture of aromatic hydrocarbons) with the aid of $AlCl_3$ [7–9]. However, Rey Boero and Wargon [10,11] and Fernadez et al. [12] found that most of the $AlCl_3$ was retained in the pitches and complete recovery of the catalyst was not achieved. The $AlCl_3$ stayed in the pitch and tended to deteriorate the quality of the resultant carbon fibers [13]. To obtain high purity product, HF-BF_3 was used to replace $AlCl_3$ as a catalyst to promote the Friedel–Craft reaction [13]. However, the use of HF-BF_3 required very special equipment and protection because of serious corrosion.

In previous works, the emphasis was on recovering catalyst from the product or minimizing the impact of catalyst retained, little attention has been given to the influence of retained catalysts on the final products. The carbon composites doped with zirconium

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http://dx.doi.org/10.1016/j.msea.2012.06.035

compound have exceptional properties. The oxidization of ZrC and the melting of ZrO_2 can effectively reduce the ablation rate of composites [14,15]. Introducing a Zr compound into C/C composites using in situ densification processes with a Zr compound catalyst may be a good method. In the present work, the ZrO_2 doped C/C composites were produced using a multiple in situ densification process in the presence of zirconium chloride. The transformation of $ZrCl_4$ during the densification process and the influence of the catalyst on the composite properties have been investigated. To understand the influence of the catalyst better, high levels were used (13 wt.% and 20 wt.%). Pitches at different soak time were examined to monitor the pyrolysis process and mesophase transformation in the presence of $ZrCl_4$. The ZrO_2 retained in the pitches and composites could be a precursor of ZrC after further treatment.

2. Experimental

2.1. Raw materials

Two types of preform were used in the study, namely low density and high density preforms. The high-density preforms were three-dimensional (3D) pitch-based C/C composites (45 mm × 35 mm × 10 mm). The low-density preforms were 3D orthogonal arrays of felt from carbon fiber bundles (PAN-based carbon fiber (T300)), sized 55 mm × 35 mm × 15 mm. Anthracene (Alfa Aesar, purity >90 wt.%) was used as the precursor monomer. Anhydrous zirconium chloride (Strem Chemical, purity >99.5 wt.%) was chosen as the catalysts without further purification.

2.2. Densification process

In each cycle a mixture of 70 g anthracene and 13 or 20 wt.% (all concentrations are expressed in weight percentage of total reaction mixture) $ZrCl_4$ were placed in a reactor. A preform was also placed in the reactor such that it was submerged once the anthracene had melted. The reactor was washed with nitrogen to provide an inert gas atmosphere and sealed and pressurized with nitrogen to 1.5 MPa. The temperature was raised from room temperature at a heating rate of 5 °C/min to 200 °C and then 2 °C/min to 350 °C. The reactor was held at this temperature for 5 h. The quenched samples, both composites and pitches, were oxidized at 220 °C for 24 h in an oven with a gentle flow of air. After oxidation, samples were carbonized in tube furnace under a nitrogen flow of 250 ml/min from room temperature to 600 °C at a rate of 1 °C/min, and then to 1000 °C at a rate of 3 °C/min, at which point the temperature was held constant for 90 min. After carbonization, two rectangular bar samples (about 45 mm × 10 mm × 5 mm) were cut from the composite. The remnant bulk sample was used for the next cycle.

The prepared composites were labeled HC/LC-*X*-*T*, in which HC and LC mean the original carbon preform with high and low densities, respectively; *X* indicates the content of $ZrCl_4$ in the feedstock and *T* indicates the densification cycles. For example, the low density preform, after three densification processes using anthracene and $ZrCl_4$ 13 wt.%, was named as LC-13-3.

The pitch samples were labeled as P-*X*-*t*, where *X* indicates the content of $ZrCl_4$ in the feedstock and *t* indicates the soaking time. For example, the products of anthracene and $ZrCl_4$ 13 wt.% at 350 °C for 5 h were named P-13-5 h.

2.3. Characterization

The bulk density of the composites was measured using the Archimedes water immersion method at room temperature. The flexure strength measurement was conducted on a universal testing machine (Instron model 1185) through a three-point flexure test. The size of the bending specimens was 45 mm × 10 mm × 5 mm and the support span was 40 mm lengthwise. The load–deflection curves were obtained by driving the crosshead at a speed of 5 mm/min and recording the load as a function of time. The fracture surfaces were investigated using ZEISS SUPRA 55 scanning electron microscopy (SEM), and a bulk cross-section profile was investigated by JOEL JSM-6701F scanning electron microscopy combined with a back-scattered electron detector (BSE).

The polarization microstructures of pitches were examined by a polarized-light microscope (Olympus BX51M). The XRD measurements were performed on Rigaku D/Max 2500 VB2+/PC. The data were collected as continuous scans, with a step size of $0.02°(2\theta)$ and a scanning rate of $10°(2\theta)$/min between 5° and $90°(2\theta)$. The ash content of the pitches was measured from 1.2 g of pitch placed in a crucible, which was then placed in a muffle. The temperature was increased from room temperature at a heating rate of 4 °C/min to 900 °C, and then held for more than 24 h.

3. Results and discussion

3.1. Effect of $ZrCl_4$ addition on the formation and transformation of mesophase

Polarized-light micrographs of the mesophase pitches, obtained from condensation of anthracene in the presence of $ZrCl_4$ at 350 °C for 0 h and 5 h, are shown in Fig. 1. P-20-0 h contains individual mesophase spherules with diameters from a few microns to about 40 μm (Fig. 1(a)), while P-13-0 h exhibits much fewer and smaller spherules (Fig. 1(c)). During the stage of heating up (200–350 °C), the viscosity of melted anthracene initially decreases with increasing temperature, and the melted feedstock efficiently flows and penetrates void space in the preform through capillary forces. After reaching a minimum level, the viscosity begins to increase because of poly-condensation. On reaching 350 °C, anisotropic mesophase spherules are formed (Fig. 1(a) and (c)). During this multiphase stage, the viscosity of the pitch is still sufficiently low to permit flow and rearrangement of the mesogenic molecules [16]. As the soaking time is elongated, coarseness and structural rearrangement are clearly evident, as illustrated in Fig. 1(b) and (d). The mesophase spherules tend to coalesce and lead to the formation of domain textures in P-13-5 h and P-20-5 h. When holding at 350 °C, further poly-condensation leads to increased viscosity due to continuing development of molecular growth processes [17,18], which in turn reduces the penetrability of the polymerization product into the composite and locks gas produced by pyrolysis. Optical observations also reveal that both the higher amount of $ZrCl_4$ in anthracene and the longer soaking time can accelerate the condensation of aromatics, developing the formation and transformation of mesophase.

Fig. 2 shows the diffraction patterns of P-13-5 h and P-20-5 h before and after carbonization. For each sample before carbonization, there is a peak (0 0 2) of graphite at $2\theta \approx 25°$ and a less defined (1 0 0) band at $2\theta \approx 43°$. Meanwhile, there is also a band for values of 2θ lower than the graphite peak (0 0 2), which indicates carbonaceous precursors, and this band is named the γ zone [19]. The peak (0 0 2) is due to the layering of the polyaromatic mesogens constituting the mesophase, whereas the γ zone is associated with the isotropic material. Although the polarized-light micrographs in Fig. 1(b) and (d) show high mesophase content, the γ zone suggests the existence of small intermediate pre-mesogenic structures and isotropic material. All samples have a significant decrease in the γ zone after carbonization, because of the progressive elimination or transformation of the isotropic fraction after carbonization [19].